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Sensitivity of peatland litter decomposition to changes in temperature and rainfall

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ABSTRACT

Changes to climate are projected over the next 50 years for many peatland areas. As decomposition of peat-forming vegetation is likely to be intrinsically linked to these changes in climate, a clear understanding of climate-peat dynamics is required. There is concern that increased temperature and decreased precipitation could increase the rate of decomposition and put the carbon sink status of many peatlands at risk, yet few studies have examined the impact of both climatic factors together. To better understand the sensitivity of peatland decomposition to changes in both temperature and precipitation and their interaction, we conducted a short-term laboratory experiment in which plant litters and peat soil were incubated, in isolation, in a factorial design. Treatments simulated baseline and projected climate averages derived from the latest UK climate change projections (UKCP09) for Exmoor, a climatically marginal peatland in SW England. Regular carbon dioxide flux measurements were made throughout the simulation, as well as total mass loss and total dissolved organic carbon (DOC) leached. The largest effect on carbon loss in this multifactor experiment was from substrate, with *Sphagnum*/peat releasing significantly less C in total during the experiment than dwarf shrubs/graminoids. Climate effects were substrate specific, with the drier rainfall treatment increasing the DOC leaching from *Calluna*, but decreasing it from *Sphagnum*. Partitioning between CO_2 and DOC was also affected by climate, but only for the peat and *Sphagnum* samples, where the future climate scenarios (warmer and drier) resulted in a greater proportion of C lost in gaseous form. These results suggest that indirect effects of climate through changes in species composition in peatlands could ultimately turn out to be more important for litter decomposition than direct effects of climate change from increased temperatures and decreased rainfall.

1. Introduction

Northern peatlands are an important carbon store, holding around one third of the global soil carbon stock (Gorham, 1991). For peatlands to accumulate organic matter, and thus sequester carbon from the atmosphere, the overall loss of carbon from the system through the combined decomposition of plant litter and peat must be lower than C input via litter production and vascular plant root exudation (Frolking et al., 2010; Limpens et al., 2008). Decomposition is the breakdown of organic matter. It can be due to one or a number of physical, chemical or biological processes. Carbon dioxide (CO_2), dissolved organic carbon (DOC), nutrients and stable hummus are among the principal final products of decomposition (Bragazza et al., 2009). Carbon is primarily lost as CO_2 in peatlands (Billett et al., 2010). However, additional losses in the form of methane (CH_4), produced during anaerobic decomposition, and DOC to aquatic systems can be an important component of the peatland carbon balance in some areas (Koehler et al., 2011). The speed and final product of the decomposition process is dependent on the chemistry of the organic matter, and the environment in which it decomposes (Limpens et al., 2008).

Understanding how peat and plant litter decomposition could be affected by climate change, specifically changes in temperature and rainfall, is key to an improved understanding of how the peatland carbon source/sink status could change during the 21st century.

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Northern peatlands are typically dominated by remains of mosses of the genus *Sphagnum*, a bryophyte (Turetsky, 2003). *Sphagnum* has played an important role in peatlands becoming such a large carbon sink. Not only does the recalcitrance of its litter mean that it keeps C in the system for longer, but the presence of *Sphagnum* maintains acidic, nutrient poor conditions which make it difficult for plants with more labile litter to establish themselves (van Breemen, 1995). Climate change may alter vegetation types in peatlands with vascular plants becoming more dominant (Buttler et al., 2015; Dieleman et al., 2015; Fenner et al., 2007; Weltzin et al., 2003). However, many ongoing catchment management programmes aim to encourage *Sphagnum* species over vascular plants as part of peatland restoration programmes (Grand-Clement et al., 2013).

While some authors have studied the effects of climate variables on the treatability of water from different peatland plant species (e.g. Ritson et al., 2014; Tang et al., 2013), little work has so far been conducted on the total flux of carbon and the partitioning between gaseous and fluvial losses from different peatland plant species. This partitioning is an important parameter to include in carbon cycle models, particularly for climate change modelling as there is likely to be a lag between DOC release from the soil and its incorporation into the atmospheric pool, as in-stream processing can lead to the temporary storage of C within the aquatic system (Hope et al., 1994). An understanding of partitioning of carbon losses between aquatic and gaseous fractions from different vegetation sources is also important for predicting whether catchment management programmes aimed at restoring certain species have the desired holistic effects of improving drinking water quality (including enhanced C sequestration) and do not result in environmental problem-shifting.

Decomposition of litters in the field is traditionally measured using the litter bag technique (Bragazza et al., 2009; Wieder and Lang, 1982). Litter of a known mass is enclosed in mesh bags with openings large enough for decomposers to access the food source, but small enough to prevent the physical loss of litters. Samples are incubated in the field, either on, or just below the soil surface (Johnson and Damman, 1991; Moore et al., 2007) and decomposition rate is quantified via mass loss or changing nutrient quotients of the litter (Keuskamp et al., 2013). In situ litter decomposition studies, using this technique, have suggested multiple drivers for increased decomposition rates in peatland systems including: elevated nutrient additions (Bubier et al., 2007), water-table drawdown (Straková et al., 2012), litter quality (Limpens and Berendse, 2003) and temperature (Moore et al., 2007). However, these field-based studies are limited to a single measure of decomposition; mass loss. Mass loss gives a valuable measure of net decomposition, which can be useful for comparing between litters, but does not provide information on the final product of the decomposition process. Carbon dioxide and DOC not only represent different flux pathways (gaseous versus aquatic), but can also be indicative of different processes and stages of decomposition. CO_2 is in effect representative of fully utilised carbon, whereas DOC could be stored in the peat column or utilised by microbes and exported to the atmosphere via respiration (Pastor et al., 2003; Turetsky, 2003).

Laboratory incubations of peatland litters to examine the relationship between decomposition and climate have been limited to date. Studies that have been conducted have tended to concentrate on a single measure of decomposition, have focussed solely on peat rather than vegetation, or have just looked at one environmental variable, such as temperature (e.g. Neff and Hooper, 2002; Moore et al., 2008) or water table (e.g. Freeman et al., 1993), in isolation. The effect of interactions between changes in temperature and rainfall on the decomposition of peatland litter is not currently well understood (Breeuwer et al., 2008). A gradient based mesocosm study measured increased C soil respiration in mesocosms transplanted to a warmer, drier location (Bragazza et al., 2016). However, isolating the effects of climatic variables such as temperature and rainfall from other confounding variables can be difficult in the field as these factors naturally co-vary. It is also difficult to separate the effects on different litters and measure the relative decomposition from different sources in the field or in intact mesocosms. To address this, previous studies have incubated soils or litters from wetland sites in isolation, notably Moore and Dalva (2001), Neff and Hooper (2002) and Wickland et al. (2007). This was the approach taken here.

A better understanding of the sensitivity of different peatland litters to changes in temperature and rainfall regime is needed to enable predictions of the impact of climate change on the stability of peatland carbon stocks, and to support better parameterisations of models that simulate past, current and future climate (Frolking et al., 2010; Smith et al., 2010). Therefore, the objectives of this research were as follows: (1) assess how litter decomposition rates varied between common ombrotrophic peatland plant species (*Calluna vulgaris*, *Molinia caerulea*, *Sphagnum* moss, and mixed litter) compared to peat; (2) determine the relative importance (or partitioning) of gaseous (i.e. CO_2) versus aquatic (DOC) fluxes during decomposition with respect to plant species and peat; (3) evaluate the importance of simulated temperature and rainfall changes on controlling total decomposition, C fluxes and partitioning between CO_2 and DOC. This final objective links to another study (Ritson et al., 2014), which used the same experimental treatments to examine the impact of climate change on the treatability (for potable water supply) of dissolved organic matter.

2. Methods

2.1. Field site and sample collection

In the south-west UK, blanket peat covers large parts of the upland areas and constitute an important store of C (Parry and Charman, 2013). These blanket peatlands represent the southern-most blanket peat in the UK and are considered climatically marginal (Clark et al., 2010). The shallow peat of Exmoor was heavily damaged by intensive drainage during the 19th and 20th centuries, and recent efforts have been made to restore large areas through a programme of ditch blocking (Grand-Clement et al., 2014, 2013). The field sites are dominated by *Molinia caerulea* (purple moor grass) (Gatis et al., 2015) and are classified as UK National Vegetation Classification M25: *Molinia caerulea-Polentilla erecta* mires (Rodwell, 1991). Paleoecological studies indicate that purple moor grass expansion corresponds with the industrial revolution and prior to this, *Sphagnum* was more dominant species within this region (Chambers et al., 1999). Exmoor typically receives precipitation of around 1800–2600 mm yr^{-1} with mean winter and summer temperatures of between 4.5–5.5 °C and 10–12 °C, respectively (Met Office, 2016). Exmoor receives a relatively high input of nutrients through atmospheric deposition, and the mean deposition of total nitrogen and oxidised sulphur for the period 2008–2012 was estimated to be 15.5–16.16 kg N h^{-1} yr^{-1} and 4.41–4.86 kg S h^{-1} yr^{-1}, respectively (DEFRA, 2015).

Samples of vegetation and peat were collected from two catchments, Aclands (51° 07′54.2″ N 3° 48′43.3″ W) and Spooners (51° 07′23.3″ N 3° 45′11.8″ W), within Exmoor National Park, UK, during July 2013. A further description of these field sites, including maps, can be found in Grand-Clement et al. (2014) and Luscombe et al. (2015). Five different substrates were collected: *Calluna*, *Molina* and *Sphagnum*, mixed litter and peat. Fresh leaves and branches were collected from *Calluna vulgaris* and *Molinia caerulea*, avoiding any plants which had been partially eaten by herbivores. Mixed litter (predominantly *Molinia caerulea* but also some *Eriphorum vaginatum*, both at the early stages of decomposition) was collected from the bog surface. Intact *Sphagnum* spp. sods (entire plants) were collected from the centre of stands and peat was collected from the top ca. 30 cm of the soil profile using a screw auger. The samples were transported back to the laboratory in cool boxes within 8 h of collection, and stored at 4 °C prior to their preparation. Sample collection is described fully in Ritson et al. (2014).

Table 1
Organic matter properties for peatland vegetation and peat classes used in the experiment. Values are means (n = 5) of subsample values, numbers in brackets are the standard error of the mean. Aromaticity is a qualitative measure and was calculated from cross polarization-magic angle spinning nuclear magnetic resonance (CP-MAS NMR).

Class	Dominant substrate	C (%)	N (%)	C:N ratio	Moisture content (g g dry wt^{-1})	Aromaticity (%)
Calluna	*Calluna vulgaris*	49.3 (0.02)	1.35 (0.01)	36.4 (0.22)	1.90 (0.01)	8
Mixed litter	Senesced *Molinia c*	45.9 (0.01)	1.29 (0.01)	35.6 (0.28)	5.38 (0.11)	5
Molinia	*Molinia caerulea*	45.5 (0.02)	2.34 (0.02)	19.5 (0.13)	3.56 (0.05)	5
Peat	Peat	29.1 (0.02)	1.64 (0.01)	17.7 (0.07)	6.06 (0.06)	11
Sphagnum	*Sphagnum* spp.	41.8 (0.03)	1.00 (0.01)	42.1 (0.28)	15.02 (0.15)	7

2.2. Sample preparation

Samples from each vegetation class (*Calluna vulgaris*, *Molinia caerulea*, mixed litter and *Sphagnum* spp.), were cut into 2–3 cm sections and mixed thoroughly within their class. Any material not from the target group was removed. Once sorted, cut and homogenised, the vegetation samples were left to air-dry in the laboratory to constant mass (Moore et al., 2007). The structure of peat is permanently altered when dried, becoming hydrophobic (Holden and Burt, 2002). For this reason, the peat was treated differently to the other substrates and was kept refrigerated and at field moist conditions prior to the experiment.

Air-dried sub-samples of each plant species and field moist peat (n = 5) were oven dried at 70 °C for 24 h to determine an air-dry to oven-dry conversion factor. This conversion factor was applied to estimate the oven-dry weight of samples at the beginning of the simulation. These oven-dry samples were analysed for litter quality (see Methods below; Table 1).

2.3. Experimental design

2.3.1. Experimental set up

Polypropylene Buchner funnels (Thermo Scientific, USA) were filled with approximately 2 g dry-weight of air-dry vegetation or 10 g homogenised peat. The stem of the funnel was packed with acid washed glass wool to ensure no loss of particulates, and each Buchner funnel was placed above an amber-glass bottle to collect leachate, for separate analysis (see Ritson et al., 2014). The climate control facilities comprise two versatile environmental test chambers (Panasonic MLR-352H). The incubators were set to cycle between 12 h at the mean daily maximum and 12 h at the mean daily minimum temperature. Deionised water was applied in amounts equivalent to the monthly rainfall, with a dispenser set to the required volume based on the area of the Buchner funnel top. This was applied gradually and evenly, over approximately 30 s, taking care not to disturb the samples.

2.3.2. Experimental design

The experiment was set up as a factorial ANOVA design, where substrate, temperature and rainfall were the treatment factors in a 5 × 2 × 2 design. Five replicates of each treatment were conducted, giving a total of 100 samples (see Ritson et al., 2014). Climate data were obtained from the UK climate projections website http://ukclimateprojections.metoffice.gov.uk/ (© UK Climate Projections 2009; UKCP09). Climate treatments were based on (i) baseline (1961–1990) mean minimum and mean maximum daily temperature and mean rainfall totals for July and August for Exmoor National Park, UK, and (ii) a projection from the UKCP09 high emissions scenario for 2080s (2070–2100). All four possible combinations of baseline and projected temperature and rainfall were applied as treatments. Mean minimum daily temperatures were set to 11.0 °C (± 0.3 °C for test chamber error) for the baseline, and 15.4 °C (± 0.3 °C) for the UKCP09 treatment. Mean maximum daily temperatures were set to 18.2 °C (± 0.3 °C) for the baseline treatment and 23.7 °C (± 0.3 °C) for the UKCP09 treatment. Rainfall totalled 100.9 and 117.5 mm for the baseline treatment for July and August, respectively, and 75.4 and 67.2 mm for the UKCP09 treatment. Overall, this was equivalent to a ca. 5.0 °C increase in temperature and ca. 35% decrease in rainfall for the UKCP09 treatments. The relative humidity (to program the test chambers) and number of rain days were set at mean values from the baseline period for all samples (for relative humidity: 80% in July, 79% in August; for rain days: 12 in July and 14 in August). The rainfall total for each month was split evenly between the rain days (resulting in irrigation amounts ranging between 4.2 mm and 8.4 mm per event, or 19 and 38 ml, depending on treatment and month), and the amounts were applied every 2–4 days. The conversion from mm to ml was based on the area of the funnel.

2.4. Measurements

2.4.1. Carbon dioxide evolution

At eight points during the experiment (on days 2, 7, 10, 17, 31, 45, 50, and 60 after the start of the incubation) samples were analysed for CO_2 efflux. Samples were taken out of the incubators individually and the top part of the Buchner funnel, containing the sample, was removed and placed into an airtight container (Lock&Lock, South Korea) which was connected to an infra-red gas analyser, IRGA (8100A, LI-COR, USA). Samples were removed for measurement in a random order to avoid the introduction of systematic measurement error. Observations with the IRGA lasted for 2 min during which time the concentration of CO_2 in the chamber (water vapour compensated) was measured every second, and the samples were out of the incubators for a maximum of 5 min. The rate of change in CO_2 concentration in the headspace during the 2-minute measurement period was used to calculate the instantaneous flux by applying a linear regression. The IRGA system was allowed to purge for a minute between samples, and a 30 second deadband (a period where the IRGA is running without the measurements being used in the flux estimate) was introduced at the beginning of each measurement to allow for adequate mixing of air in the headspace. The CO_2 time series for each sample was analysed separately, and the deadband was adjusted where necessary. All flux estimates were derived from a minimum of 60 consecutive CO_2 concentration measurements (i.e. 60 s). Individual flux estimates were converted to mg CO_2-C gC^{-1} day^{-1}. Cumulative CO_2 flux over the course of the two month experiment was calculated for each sample based on a linear interpolation of fluxes between the successive measurements (Neff and Hooper, 2002), expressed as mg CO_2-C gC^{-1}.

2.4.2. Dissolved organic carbon

DOC analysis was performed on the cumulative leachate collected at the end of the simulation period. Samples were filtered through a GF/F filter (Whatman, UK) with a nominal pore size of 0.7 µm, acidified to ~pH 2 with HCl and stored at 4 °C prior to analysis. Organic carbon content was measured as non-purgeable organic carbon (NPOC) using a total organic carbon analyser (Shimadzu TOC-V, Japan). Calibration and quality control checks were run daily from freshly prepared standards and samples were analysed within one week of the end of the simulation. Organic carbon concentration (mg L^{-1}) was converted to DOC leached (mg) based on the volume of leachate collected. As temperature and rainfall treatment affected the volume of sample collected,

this was then reported as mg DOC–C gC^{-1}, based on the starting dry mass and initial C content of each sample.

2.4.3. Mass loss

At the end of the two-month incubation period, samples were removed from the incubators, dried at 70 °C for 48 h and weighed. C loss was estimated based on the starting mass and starting C content, as well as the end mass and end C content. This was expressed as mgC gC^{-1}.

2.5. Litter quality analysis

The oven-dry subsamples from the beginning, and all samples from the end of the experiment were ground using a laboratory disc mill with an agate barrel (Tema Machinery Ltd., UK) and analysed for total C and N (Thermo FLASH 2000 elemental analyser). The handling and analysis of samples were undertaken together with reference material (Pahokee Peat, International Humic Substances Society) in order to verify the calibration and quality of the results. Subsamples from the start of the experiment were also analysed for C character using nuclear magnetic resonance (NMR) analysis. Cross polarization-magic angle spinning (CP-MAS) ^{13}C NMR analysis was undertaken at the University of Reading chemical analysis facility (CAF) on a Bruker AV500 instrument based on the method of Wong et al. (2002). This technique is used widely in environmental studies and is good for looking at relative changes in carbon distribution across a series of samples (Simpson et al., 2011). For the vegetation samples 1024 transients (executions of the pulse sequence) were taken, however due to the presence of paramagnetic material in the peat soil transients were increased to 4096 to improve the signal to noise ratio. Magic angle spinning (MAS) spin rate was set at 10 kHz to shift spinning side bands out of the region of interest and all signals were externally referenced to adamant. The aromatic peak between 110 and 140 ppm was integrated and its percentage of the total signal calculated to give an indication of the differences between relative aromaticity between samples (Peuravuori et al., 2003), which can be used as an alternative qualitative measure of the recalcitrance of the litter (see Table 1). For further reading on using NMR analysis for environmental research, see Simpson et al. (2011).

2.6. Statistical analysis

All statistical analyses were carried out using R version 3.0.2 (R Core Team, 2015) and plots were generated using the ggplot2 package (Wickham, 2009). The experiment involved a three-way analysis of variance (ANOVA) design where temperature, rainfall and substrate were the experimental factors. The effect of these factors, and their interaction, on response variables of CO_2 flux, mass loss, DOC leached and CO_2:DOC ratio production was analysed (Table 2). A Fligner-Killeen test was performed to determine that there was equal variance between groups, and residuals were checked for normality. Carbon dioxide flux, DOC flux and CO_2:DOC ratio were all square-root transformed prior to inclusion, in order to meet the assumption of normally distributed residuals. A critical value of $P = 0.05$ was used for statistical significance. For multiple comparisons, the Tukey honest significant differences (HSD) test was used. The variance explained by each factor was estimated using omega-squared (ω^2), a test which is suitable for estimating effect size from small sample sizes (Keselman, 1975).

3. Results

3.1. Variability of decomposition rates between different substrates

Decomposition was greatest for the *Molinia* samples and slowest for the peat samples (Fig. 1). The same substrate rankings were evident in terms of the following: the estimated cumulative CO_2 flux (means ranged from 942.87 mgC gC^{-1} for *Molinia* to 41.26 mgC gC^{-1} for peat; Fig. 1); the DOC flux (means ranged from 20.95 mgC gC^{-1} for *Molinia* to 1.07 mgC gC^{-1} for peat; Fig. 1); and the overall total measured mass loss (means ranged from 511.21 mgC gC^{-1} for *Molinia* to 27.43 mgC gC^{-1} for peat; Fig. 2). Substrate was a significant explanatory factor in the ANOVA for all of these response variables ($P < 0.001$; Table 2). Post-hoc tests suggested significant differences in the order *Molina* > *Sphagnum* = Mixed litter > *Calluna* > peat for CO_2 flux; *Molinia* > *Calluna* = Mixed litter > *Sphagnum* > peat for DOC flux; and *Molinia* > *Calluna* > *Sphagnum* = Mixed litter > peat for mass loss.

Table 2
ANOVA model results, where the model fitted is *response* = Temperature * Rainfall * Substrate (cumulative CO_2, DOC and CO_2:DOC ratio are square-root transformed data). Significant differences ($P < 0.05$) are highlighted in bold and effect sizes (ω^2) are stated in brackets. "Temp", "Rain" and "Sub" are short for Temperature, Rainfall and Substrate, respectively.

Variable	Factor	*F*	df	*P* value
Cumulative CO_2 ($mgCO_2$-C gC^{-1})	Temperature	1.04	1	0.311
	Rainfall	3.25	1	0.075
	Substrate	631.08	4	< **0.001** (0.960)
	Temp:Rain	0.06	1	0.804
	Temp:Sub	1.27	4	0.288
	Rain:Sub	1.68	4	0.164
	Temp:Rain:Sub	1.27	4	0.290
Mass loss ($mgCO_2$-C gC^{-1})	Temperature	20.10	1	< **0.001** (0.005)
	Rainfall	0.01	1	0.927
	Substrate	946.23	4	< **0.001** (0.966)
	Temp:Rain	0.01	1	0.915
	Temp:Sub	3.80	4	**0.007** (0.003)
	Rain:Sub	2.72	4	**0.035** (0.002)
	Temp:Rain:Sub	0.56	4	0.690
DOC ($mgCO_2$-C gC^{-1})	Temperature	18.19	1	< **0.001** (0.015)
	Rainfall	3.38	1	0.070
	Substrate	247.14	4	< **0.001** (0.838)
	Temp:Rain	0.04	1	0.837
	Temp:Sub	5.12	4	**0.001** (0.014)
	Rain:Sub	11.34	4	< **0.001** (0.035)
	Temp:Rain:Sub	4.43	4	**0.003** (0.012)
CO_2-C:DOC-C	Temperature	15.57	1	< **0.001** (0.056)
	Rainfall	26.16	1	< **0.001** (0.097)
	Substrate	19.96	4	< **0.001** (0.292)
	Temp:Rain	0.01	1	0.921
	Temp:Sub	3.27	4	**0.015** (0.035)
	Rain:Sub	8.71	4	< **0.001** (0.119)
	Temp:Rain:Sub	2.24	4	**0.072**

There was a steady decrease in CO_2 release over the entire incubation period, for all substrates and treatments. The decrease in CO_2 flux was greatest for the *Molinia* samples, with a reduction in estimated flux between the first (day 1 to 30) and second half (day 31 to 60) of the experiment of 64.27%, compared to peat where the difference was 25.13% – the lowest decline recorded.

In terms of total mass balance, the overall loss of C measured directly through mass loss of the substrate and by the total fluxes (DOC + CO_2) were not equal. While DOC fluxes were less than the total mass loss, the cumulative CO_2 flux estimated by integration across the experimental period (sensu Neff and Hooper, 2002) was greater than the total mass loss.

3.2. Carbon dioxide to DOC partitioning

The cumulative flux of CO_2 was greater than DOC for all of the samples (Fig. 1). Mean CO_2:DOC quotients ranged from 31.56 for *Molinia* to 68.67 for *Sphagnum* (all climate treatments pooled), indicating that proportionally more carbon was lost as DOC from *Molinia* than *Sphagnum*. Substrate was again the strongest factor explaining the variation in partitioning between gaseous and aquatic fluxes ($P < 0.001$). There was a significant relationship between total CO_2

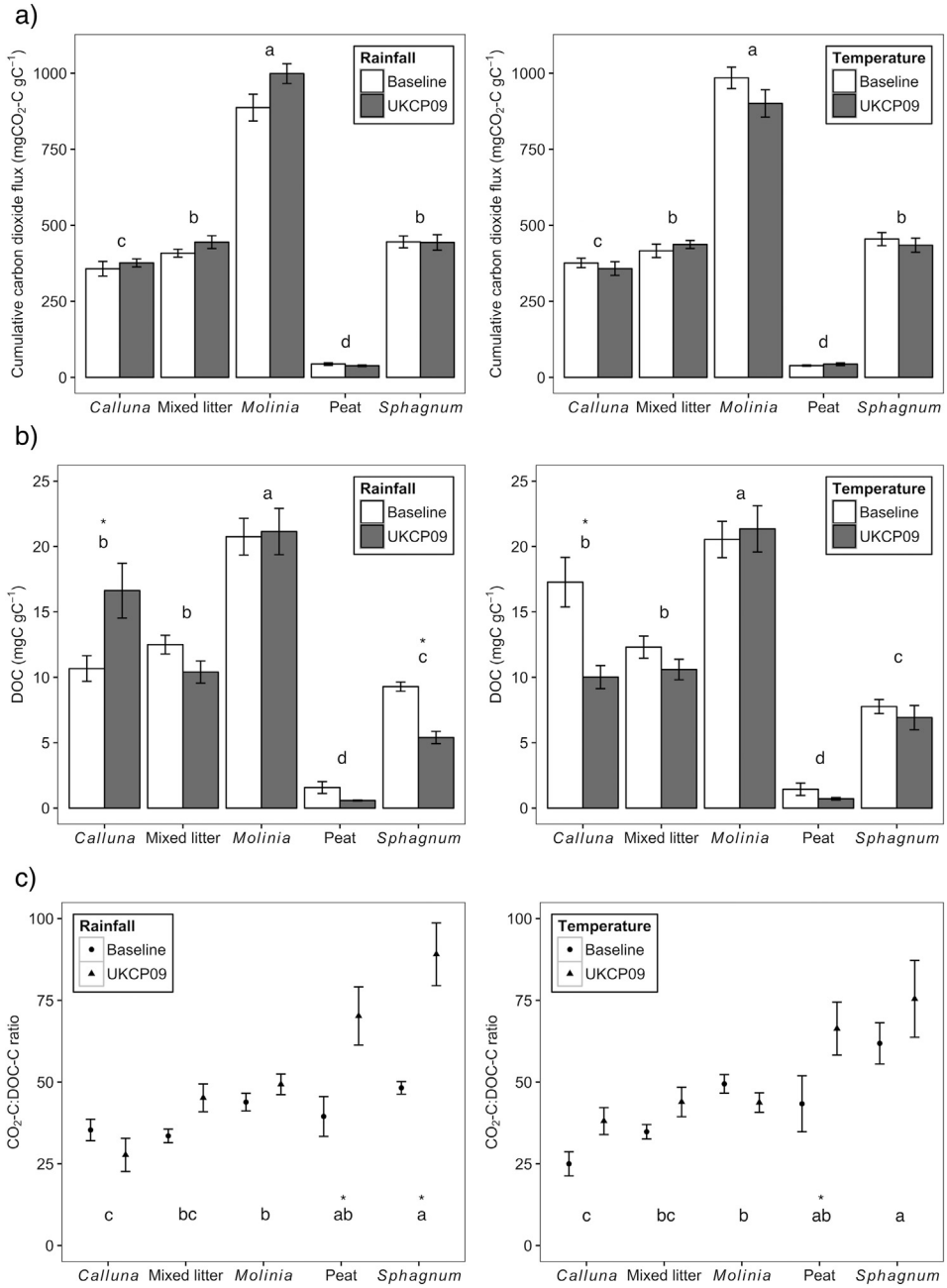

Fig. 1. Treatment effects on measures of carbon fluxes, and their ratio; (a) cumulative CO_2 flux, (b) DOC flux, (c) cumulative CO_2 to DOC ratio (error bars indicate one standard error). Different letters denote statistically significant differences in means between substrates and asterisks denote significant differences between treatments for substrates based on Tukey HSD test ($P < 0.05$).

flux and DOC leached between groups when all data were pooled, indicating that DOC leaching increases with CO_2 flux. However, this relationship was not observed within substrate groups.

The general trend was for an increase in the CO_2:DOC quotient under UKCP09 future climate scenarios (Fig. 1). There was a statistically significant interaction between rainfall and substrate ($P < 0.001$), with the proportion of C lost as CO_2 generally increasing under the UKCP09 (drier) rainfall scenario. Post-hoc tests revealed that drier conditions were only significant in changing the partitioning between gas and aquatic carbon fluxes for the peat ($P < 0.001$) and *Sphagnum* ($P < 0.001$) samples, the mean of which increased from 24.91 (± 5.74) to 78.64 (± 13.85) and from 47.34 (± 2.41) to 101.78 (± 16.25) when comparing the baseline temperature and rainfall to the UKCP09 temperature and rainfall treatments. Partitioning between CO_2 and DOC in other substrates, *Molinia*, *Calluna* and mixed litter, was unaffected by temperature and rainfall treatments ($P > 0.05$).

3.3. Relative importance and interaction between temperature and rainfall in controlling decomposition

Increasing temperature had a significant effect on decreasing DOC flux ($P < 0.001$) and increasing mass loss ($P < 0.001$). In addition, significant interactions between temperature and substrate ($P < 0.001$) and rainfall and substrate ($P = 0.001$) were seen for DOC flux and for mass loss ($P = 0.007$ and $P = 0.035$, respectively), indicating that the effect of simulated climate change depended on substrate type. For DOC, post hoc tests suggested that the interaction was only significant between temperature and *Calluna*, whereas for rainfall,

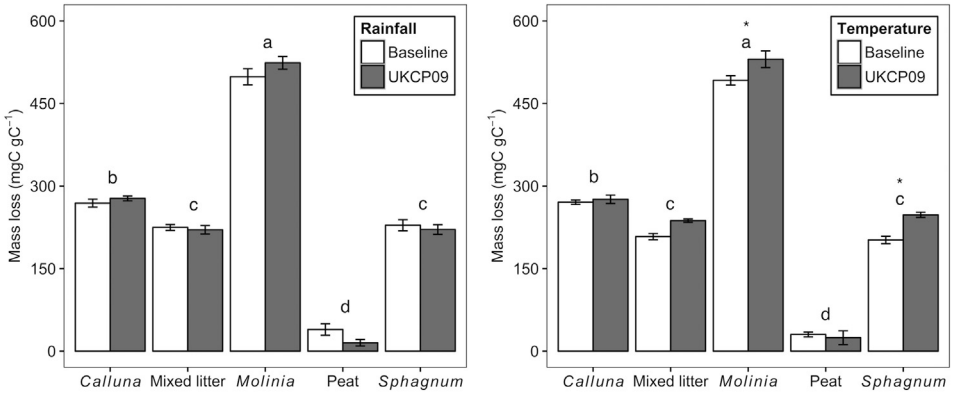

Fig. 2. Treatment effects on C loss estimated from mass and C quotient measurements (error bars indicate one standard error). Different letters denote statistically significant differences in means between substrates and asterisks denote significant differences between treatments for substrates based on Tukey HSD test ($P < 0.05$).

there was a significant interaction between rainfall treatment and *Calluna* and rainfall treatment and *Sphagnum*. This interaction between rainfall and substrate was not unidirectional, however, with the drier rainfall treatment increasing DOC in *Calluna* samples, but decreasing it in *Sphagnum*. With mass loss, only *Sphagnum* was close to being significant on its own. Differences in cumulative CO_2 flux between climate treatments (both temperature and rainfall) were non-significant ($P > 0.05$), though rainfall was close to the critical threshold ($P = 0.075$). No significant interaction between temperature and rainfall for any of the measures of decomposition was observed (CO_2 flux, DOC flux or mass loss).

4. Discussion

4.1. Carbon fluxes and decomposition rates between different substrates

The fluxes of CO_2 and DOC, and the mass loss, were lowest from the peat samples compared to litter sources, consistent with previous work (Moore and Dalva, 2001; Tang et al., 2013). Decomposition in peatland ecosystems progresses along a continuum from freshly senesced plant litter to peat. Part of the reason that peat decomposes more slowly than fresh litter is because more labile compounds are preferentially utilised by decomposers (Wieder and Lang, 1982). This results in older peat being composed of progressively more recalcitrant materials (Broder et al., 2012). In the field, these differences are likely to be even greater as decomposition of peat is further inhibited by anoxic and acidic conditions which prevail for longer at greater depths. Here, we used measures of C:N ratio and aromaticity to characterise the quality of the substrates. A high C:N ratio usually suggests recalcitrant litter, as N is limiting for microbes and can also stimulate the activity of certain enzymes (Bragazza et al., 2012). Here peat had the lowest C:N ratio, which could be due to retention of N containing compounds during the decomposition process (Kalbitz and Geyer, 2002). Aromaticity is another potential measure of decay resistance as aromatic polymers are characterised by structural and chemical recalcitrance. In this instance, peat had the highest estimated proportion of aromatic compounds (Table 1), which could in part explain its low decomposition rate relative to the other substrates.

In terms of specific fluxes, *Sphagnum* produced the least DOC in line with previous observations of high retention of carbon in this species (Fenner et al., 2004). *Sphagnum* also produced slightly more CO_2 than *Calluna*, which was unexpected given the well documented recalcitrance of *Sphagnum* litter which has been shown to decompose much more slowly than other peat forming vegetation (van Breemen, 1995). This could have been a result of environmental conditions, specifically water content, as the poor water holding capacity of *Calluna* litter meant that lack of water supply could have limited its decomposition during laboratory simulation experiments (Blok et al., 2015; Toberman et al., 2008).

The estimates of cumulative CO_2 flux were approximately double the amount estimated from C mass loss, suggesting an overestimation of cumulative CO_2 flux by integrating point measurements recorded here. This could partly be due to the measurement of some autotrophic respiration from peat roots in the earlier stages of the experiment, or an inadequate representation of night-time respiration rates. However, given that all samples were treated in the same way, and were well mixed to begin with, it is reasonable to assume that the observed differences between groups are robust.

4.2. Relative importance of gaseous and fluvial fluxes

The release of DOC during organic matter decomposition to surface waters is an important component of the peatland carbon budget (Billett et al., 2010). Little is known about partitioning between CO_2 and DOC fluxes in peatlands (Bonnett et al., 2006). Herein, it was shown that *Molinia* produced the most DOC as a proportion of its starting mass, and peat produced the least. However, in terms of the ratio of CO_2 to DOC, *Calluna* and mixed litter had the lowest ratios, signalling that a higher proportion of mass is lost as DOC than CO_2 for these substrates, when compared with the others. Again, absolute values for CO_2:DOC may not be accurate due to overestimation of measured CO_2 fluxes, but comparisons between groups should still be robust.

Previous studies have reported DOC fluxes equivalent to over 20% of net ecosystem exchange (NEE) (e.g. Dinsmore et al., 2010; Koehler et al., 2011). In some instances, DOC exported to streams has been estimated to exceed NEE (Billett et al., 2004), highlighting the importance of including this flux when estimating source/sink status of a peatland. Strong correlations have been found between gross primary productivity (GPP) and DOC concentrations in peatland catchments (Dinsmore et al., 2013; Harrison et al., 2008), suggesting a large amount of DOC is produced directly by living plants, indirectly by rhizosphere priming or by the decay of fresh plant litter. The difference in the amount of DOC released from the peat and litter samples in this study during decomposition supports the theory that the decay of fresh litter is a substantive DOC source (Evans et al., 2007; Palmer et al., 2001). In the field, a lot will depend on the regulating effect of water table depth on decomposition, flow pathways of runoff (Wallage and Holden, 2011), as well as substrate.

We observed a lower DOC flux but no significant change in CO_2 flux under the UKCP09 (warmer) temperature scenario. Combined with the lower DOC flux under UKCP09 (drier) rainfall scenario for some of the substrates (*Sphagnum*), this resulted in an increase in the partitioning coefficient between CO_2 and DOC flux for some of the substrates

(*Sphagnum* and peat), which is in accordance with the findings of Neff and Hooper (2002) in their arctic soil samples. This implies that a greater proportion of C released from *Sphagnum* and peat would be lost in the form of CO_2 than DOC under warmer and drier conditions, with the effect of rainfall being slightly stronger than temperature. The strength of the rainfall effect suggests that it is due more to the decreased flux of DOC than due to a reduction in total decomposition. The total DOC measured in this study was in effect net DOC production; a function of release and transport, as well as its mineralisation. The decreased DOC flux could be explained by a suppression of DOC mobility by drought-induced acidification (Clark et al., 2006; Clark et al., 2012). DOC production could be affected by both microbial enzymatic activity and physical leaching. It could be that DOC was produced, but lack of water supply limited physical leaching and so it was subsequently consumed by microbes present in the samples (Moore and Dalva, 2001). The findings presented here, that CO_2:DOC partitioning from *Sphagnum* and peat could be affected by climate change, but that the partitioning from other substrates was not affected, will be of interest to those modelling the response of peatland C balance as it indicates that DOC flux cannot be estimated from ecosystem respiration alone. It is also useful information for water treatment engineers who are trying to plan future climate-proof investments in treatment works, as these results imply that DOC could increase or decrease in the future, depending on the proportion of different plant species in the catchments, and the pattern of rainfall.

4.3. Effects and interactions between temperature and rainfall

Results indicate that simulated temperature changes have a greater effect on the loss of DOC (generally decreasing the flux) and on mass loss (generally increasing the flux) than on the production of CO_2. The effect varied between substrates, for example, drier conditions increased the DOC flux from *Calluna*, but decreased it from *Sphagnum*. When looking at the main drivers of increased decomposition in peatlands, other laboratory based studies have also found mixed results. Higher temperatures led to increased mass loss (between 5, 10 and 15 °C) in a one year incubation of Scots pine needles below a living moss layer (Domisch et al., 2006), supporting the results found here. Neff and Hooper (2002) also found that temperature controlled the CO_2 flux from their incubated soil samples, but the response depended largely on vegetation community. However, in their study on DOC production across a range of spatial scales, Preston et al. (2011) found that temperature had no effect on DOC production in their peat microcosm experiment, regardless of moisture treatment. This contrasts with Clark et al. (2006) who found increased DOC release at 20 °C relative to 10 °C in another laboratory study incubating peat mesocosms.

While measured mass loss did increase positively with temperature, measured CO_2 fluxes did not. Investigations at lower temperatures than those used here have suggested *Sphagnum* becomes more productive, growing faster, with increases in temperature from a low base (Breeuwer et al., 2008), but that the opposite can occur for warmer temperatures (17.5 and 21.7 °C) (Breeuwer et al., 2009). Results herein indicate that decomposition, measured through mass loss, increased with temperature, suggesting that the strength of the peatland C sink could be reduced during summer months.

Rainfall treatment was just above the $P = 0.05$ critical threshold for cumulative CO_2 ($P = 0.075$) and DOC flux ($P = 0.070$), with lower values seen under the UKCP09 (lower rainfall) conditions. For DOC in peat, this agrees with the findings of Tang et al. (2013) who found that DOC export was greater in the wetter treatments, and declined in the drought treatments. Observed responses of DOC export to drought or experimentally lowered water tables have been varied, with suggestions that DOC export could increase due to drought (Worrall et al., 2006). However, there are mechanisms which could explain the decrease in DOC observed here. Decreased DOC during droughts could be due to a suppression of DOC transport by drought-induced decrease in DOC solubility (Clark et al., 2012, 2006), or an increase in hydrophobicity (Worrall et al., 2008) rather than a change in the production of DOC through organic matter decomposition. A difference here is that this study simulated rainfall whereas those examining the mechanisms have tended to focus on water table effects, either through manipulations in the laboratory or event-based analysis in the field.

4.4. Limitations of the study

The data presented here are a useful indication of the relative importance of different substrates as sources of DOC and CO_2 fluxes, decomposition and the potential for changes in partitioning between CO_2 and DOC under future climate conditions. However, these are laboratory based simulation experiments and are subject to constraints that must be taken into account when interpreting the results. Samples may have been exposed to more extreme drying conditions than under field conditions as moisture levels were not regulated by living vegetation and/or underlying water table, and the lack of a peat substrate beneath the samples from the vegetation groups could also have increased the loss of water and so negated any rainfall treatment effect. Ritson et al. (2017) found that any exposure to oxygen (during laboratory experiments) increased DOC from peat and changed the quality of the C. The differences with the results presented here suggest a high sensitivity to the amount and frequency of the rainfall treatments. The findings of these laboratory experiments now need to be tested under field conditions.

4.5. Wider implications for our understanding of peatland carbon balances

While predictions about future rainfall patterns are variable, with both increases and decreases projected for northern latitudes (IPCC, 2014), models are in strong agreement that temperatures at mid-to-high latitudes will increase due to climate change (Murphy et al., 2009), and that drought events are likely to become more frequent (Meehl and Tebaldi, 2004). While there are differences in both magnitude and direction of change between the substrates, the data here suggest that warmer summer temperatures and decreased rainfall could increase overall decomposition, reduce the flux of DOC, and subsequently alter the partitioning of carbon released during decomposition from DOC to CO_2.

Other studies have suggested that the effect of climate change will be more through indirect effects on the composition of vegetation, with graminoids and dwarf shrubs being favoured over *Sphagnum* mosses in warmer, drier conditions (Kapfer et al., 2011; Weltzin et al., 2003). Given the greater lability of the litter produced by these plant functional types, seen here in the greater decomposition of the *Molinia* samples, this could be a concern for climate change mitigation. However, in SW England, where these samples were collected, graminoids (*Molinia*) are already highly prevalent (Chambers et al., 1999) and so the effect may not be as severe, as climate-induced vegetation change may already have occurred. The shallow peat in this area suggests the area could have been sequestering C at a lower rate than other blanket peatlands, or even losing C, though further work looking at the entire C balance is needed to verify this.

In the field, it is likely that climate change may increase productivity, and therefore litter production, alongside any increase in decomposition rates. Studies have already provided evidence that warmer temperatures can increase rates of carbon sequestration at some northern latitude peatlands, due in part to longer and warmer growing seasons enhancing plant growth (Loisel and Yu, 2013). Therefore, when interpreting the differences in decomposition rates of the different substrates in the context of in situ actual conditions, it is also important to consider their respective litter production rates and substrate supply (Ritson et al., 2016). While *Molinia* showed the fastest decomposition in this experiment, it also tends to produce more litter than *Calluna* (e.g. Aerts, 1989), so is likely to be a more significant

source of C at the catchment scale. Also, while both substrates generally produce less "litter" than *Sphagnum* (Bragazza et al., 2012), this may change in a warmer, drier climate (Breeuwer et al., 2009). Further work is needed to take into account the effect of climate change on productivity and litter production, as well as on decomposition, to assess the likely impacts of climate change on the future carbon balance of peatlands.

5. Conclusions

This study has used short-term laboratory incubations of peat and peat-forming vegetation from a climatically marginal blanket peatland in SW England in order to assess the relative importance of different temperature and rainfall scenarios for the main C fluxes (CO_2 and DOC) and their partitioning during short-term litter decay. The largest variation in C fluxes and total mass loss was seen between substrates, with smaller fluxes (cumulative CO_2 and DOC) and mass lost from *Sphagnum*/peat compared to higher fluxes and mass loss from dwarf shrub/graminoids. The CO_2:DOC ratio was lowest for *Molinia* and highest for *Sphagnum*. Climate factors were important too, but the effect depended largely on the substrate. For example, while the future (drier) rainfall scenario increased the DOC flux from *Calluna*, it had the opposite effect for *Sphagnum*. Therefore, indirect effects on species composition in peatlands could ultimately turn out to be more important than direct effects of climate change from increased temperatures and decreased rainfall.

Upscaling of this work from laboratory to field is needed in order to confirm these laboratory-based findings and improve understanding of the likely impacts of climate change on C fluxes and decomposition in peatlands. Further work across natural climatic gradients is one way of addressing this research need, deploying a space for time substitution to understand future climate change.

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